

Pulsed laser deposition of poly (L-Lactide) acid on nitinol substrate

R. H. CIMPOESU*, G. O. POMPILIAN^a, C. BACIU, N. CIMPOESU, C. NEJNERU, M. AGOP^b, S. GURLUI^c, C. FOCSA^a

**"Gh. Asachi" Technical University, Faculty of Materials Science and Engineering, Iasi, Romania*

^aLaboratoire de Physique des Lasers, Atomes et Molécules (UMR 8523), Université Lille 1 Sciences & Technologies, 59655 Villeneuve d'Ascq cedex, France

^b"Gh. Asachi" Technical University, Department of Physics, Iasi, Romania

^c"Al. I. Cuza" University of Iasi, Faculty of Physics, Iasi, Romania

Shape memory alloys (SMAs), especially those based on Ni-Ti, have important applications in the medical field. Growing thin biodegradable polymer layers on the SMAs surface improves their corrosion resistance, biocompatibility and applicability as well. Using the pulsed laser deposition method, thin layers of biodegradable polymer PLLA (Poly-L-Lactide Acid) were deposited on nitinol substrates. They were subsequently studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

(Received November 15, 2010; accepted November 29, 2010)

Keywords: Nitinol, Pulsed laser deposition, Thin layers

1. Introduction

The biodegradable polymer poly(l-lactic acid) (PLLA) is widely used to construct cell scaffolds for tissue engineering purposes due to its excellent biocompatibility, as it can degrade into lactic acid and be eliminated from body by normal metabolic pathway [1]. Poly-L-lactide (PLLA) is the product resulting from polymerization of L, L-lactide (also known as L-lactide). PLLA has a crystallinity of around 37%, a glass transition temperature between 60-65 °C, a melting temperature between 173-178 °C and a tensile modulus between 2.7-16 GPa [2].

The material properties permit its use in medicine applications to protect the human body from contact with unwanted materials for example nickel release by corrosion or electro-corrosion [3].

Wide ranges of shape memory alloys (SMAs) are known. Among them, only three alloy systems, namely NiTi-based, Cu-based (CuAlNi and CuZnAl) and Fe-based, are presently of greater commercial importance.

The NiTi-polymer-composites shape memory materials are of special interest in medical applications due to the large obtainable strains, the constant stress level and their biocompatibility. They are used for novel applications mainly in orthodontics, medical instrumentation or mechanical engineering [3-5, 6, 7].

NiTi- SMAs thin films composites have the potential to substantially reduce those forces compared to conventional NiTi wires and tubes. In orthodontic applications lowering the forces during archwire treatment is of special importance due to tooth root resorption, which can be caused by the application of oversized forces.

SMAs thin-film deposition may be obtained using various well known physical technologies (i.e. thermal evaporation, magnetron sputtering and pulse laser deposition).

In order to obtain both a high corrosion resistance, improving the biocompatibility, to obtain a good compactness, uniform, pure and dense layer surface, but also to keep the chemical composition (stoichiometric) of the bulk material, pulse laser deposition technology (PLD) is mostly used [8, 9]. Moreover, the Pulsed Laser Deposition (PLD) is gathering interest due to its versatility and controllability.

PLD is a thin film deposition technique where a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited, in our paper- a bulk PLLA material. This material is vaporized from the target (in a plasma plume) which deposits it as a thin film on a substrate (such as a Ni-Ti shape memory alloy under wire round form). This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the grown films.

While the basic-setup is simple relative to many other deposition techniques, the physical phenomena of laser-target interaction and film growth are quite complex [10-12]. Under the laser-matter interaction, the ejected plasma plume into the surrounding vacuum contains many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten droplets, before depositing on the substrate. A thorough investigation of the complex laser-sample interaction seems necessary, in terms of ejected products, nature of the desorption process

itself, and/or the specific response to different parameters involved, like pulse energy [10] or wavelength [11, 12] of the exciting laser beam.

In order to obtain a shape memory, nitinol substrate and microstructures, some preliminary studies in a new PLD-experimental set-up will be discussed.

2. Experimental details

A schematic view of the experimental set-up is given in Fig. 1. The fourth harmonic ($\lambda = 266$ nm) of a 10 ns

Nd:YAG pulsed laser beam (Continuum Surelite) has been focused by a $f = 25$ cm lens onto a polymer target placed in a vacuum chamber (evacuated to 10^{-2} Torr) [10]. The laser impact spot is elliptical (45° incidence) with an estimated area of ~ 0.4 mm². The laser beam energy has been continuously monitored by an OPHIR joulemeter. The energy usually employed was 25-30 mJ/pulse, which leads to a typical laser intensity of ~ 1 GW/cm².

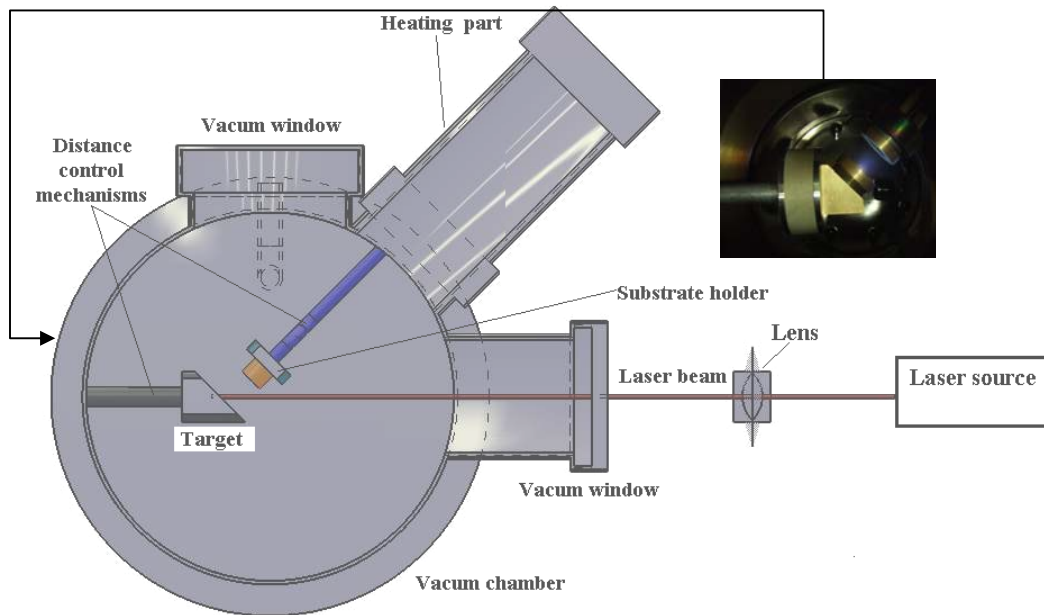


Fig. 1. Experimental set-up.

The alloy used as substrate in this study is manufactured by Saes Getters Group, USA, and is a shape memory material whose characteristics are presented in Table 1, for 700 μ m diameter wire. The deposited thin

layer was obtained by PLD process from a bulk sample of PLLA (Lactel Biodegradable Polymers, Birmingham U.S.A.) having the inherent viscosity of 0.95 dL/g in CHCl_3 .

Table 1. Properties of Ni-Ti superelastic wire [6].

As (Fully annealed) – Af	°C	-15 90
Nominal Loading plateau stress@3% strain, in Austenite		500 MPa, 72,500 psi
Nominal Ultimate Tensile Strength in Austenite		1250 MPa, 181,000 psi
Max. Residual elongation after 8% strain in Austenite [%]		0.5
Main Applications		Guide wires, Stents, Arch wires, Implantable devices, Embolic Protection
Mechanical treatments:		- Cold drawn, Superelastic, Trained
Typical impurity content in wt:		- O < 250 ppm: C < 250 ppm: Total all others < 1000 ppm
Standard Cut-length:		± 0.007 " (0.18mm) for L < 12" (0.3m)
Tolerances:		$\pm 0.2\%$ of specified cut-length for L > 12" (0.3m)

The polymer target is moved in XY plane by a micrometric manipulator in order to expose a fresh area to the laser beam. The unheated substrate is kept fixed and is parallel to the target surface. The target-substrate distance is 20 mm and the deposition time is 20 min.

To characterize the deposited thin films a VEGA-TESCAN Scanning Electron Microscope equipped with the QUANTAX Bruker AXS Microanalysis system has been used. The microscopy was realized with a Secondary Electron detector for different scales to present the surface wires using 10 (for polymer material) to 30 (for metallic material) kV voltage supply of electron gun tungsten

filament. The images were taken at 10 mm distance to samples, for SEM imagery and at 16 mm distance between samples and AXS detector for chemical analysis.

3. Results and discussion

The polymer microstructure in bulk shape, before the PLD process, is represented in Fig. 2 for different power amplifications obtained on a scanning electron microscope. It can be seen that the surface of the target was almost smooth and there is no crack or porosity on it.

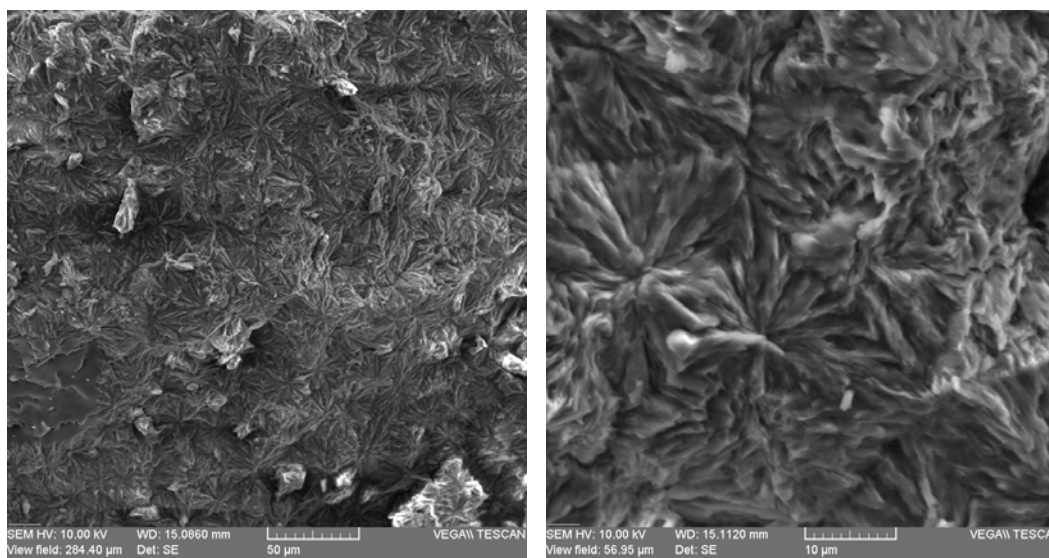


Fig. 2. SEM pictures of Poly(L lactide) acid microstructures at a) 1000 x and b) 5000 x magnification ratios.

Using the EDX, a comparative analysis of the bulk polymer versus the PLD deposited film has been performed, both qualitatively (elements energy spectrum analysis) and quantitatively (mass and atomic percentages

analysis). From EDX analysis of bulk state material presented in Fig. 3, two energy peaks (carbon and oxygen elements) with less than 0.5 keV are obtained.

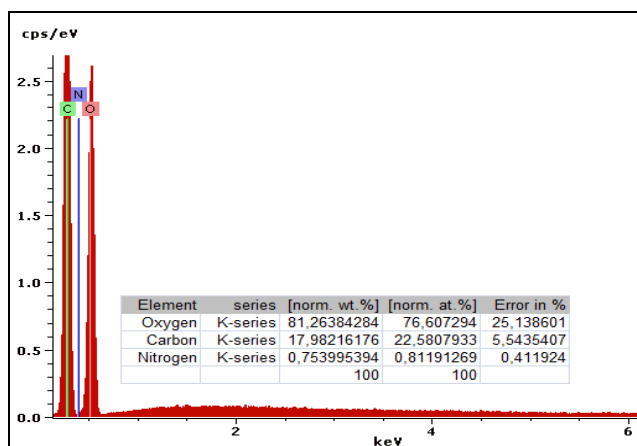
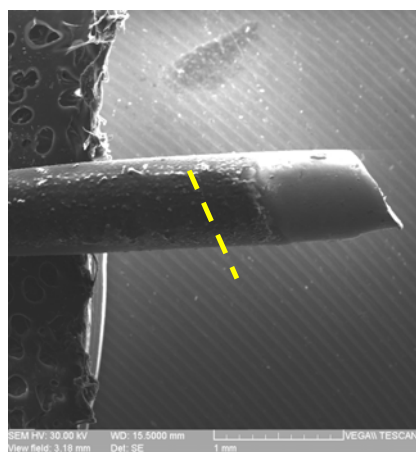


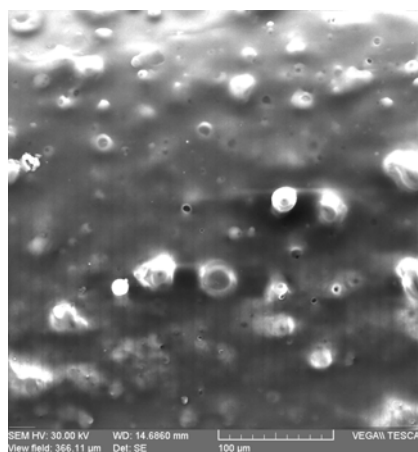
Fig. 3. Energy spectrum and chemical composition of bulk PLLA polymer.

The observed reduced percentage of nitrogen in chemical composition of bulk material over the energy spectrum may be caused by external contamination processes during material preparation or chemical testing method.

In Fig. 4a the general aspect of a nitinol wire covered (by PLD) with a PLLA polymer thin film is



a)



b)

Fig. 4. SEM images of polymer layer obtained by PLD process on a nitinol wire substrate: a) general view, the yellow line represents the bordered between covered and uncovered areas; b) detail of the deposited layer(500x magnification).

Comparing the bulk polymer structure (Fig. 2) and the polymer thin film structure (Fig. 4b) the influence of the PLD process on the microstructure is clearly marked.

Chemical composition in carbon and oxygen on the deposited layer is presented in Table 2, showing a similar 1:3 ratio between carbon and oxygen abundances in the material that was transferred from the target (PLLA) to the

substrate (NiTi alloy). The normalized weight percentages are identical (despite the large error bars) in Table 2 (thin film) and Fig. 2 insert (bulk), which is a strong argument in favor of a "soft" transfer from the target to the substrate, without alteration of the elemental chemical composition during the pulsed laser deposition process.

Table 2. Chemical composition of the PLLA polymer thin film obtained by PLD process on a shape memory nitinol alloy, as determined by EDAX.

Element	AN	series	Net	[wt.%]	[norm.wt.%]	[norm.at.%]	Error in %
Oxygen	8	K-series	19545	80.7656	80.76721	75.91868	25.4101
Carbon	6	K-series	37273	19.2324	19.23279	24.08132	5.993956
			Sum:	99.998	100	100	

In Fig. 5 relative distributions of several chemical elements: carbon, oxygen, nickel and titanium are given. In the bottom part of the picture the area selected for analysis is represented, a zone at the border between substrate and the deposited layer. The increase of carbon and oxygen elements signal on the covered area is observed.

From the 600 μm long analyzed zone, on about 400 μm the signal of the substrate (nickel and titan) appears 3-4 times smaller than in the free zone from the right part of the picture, confirming the presence of the polymer layer.

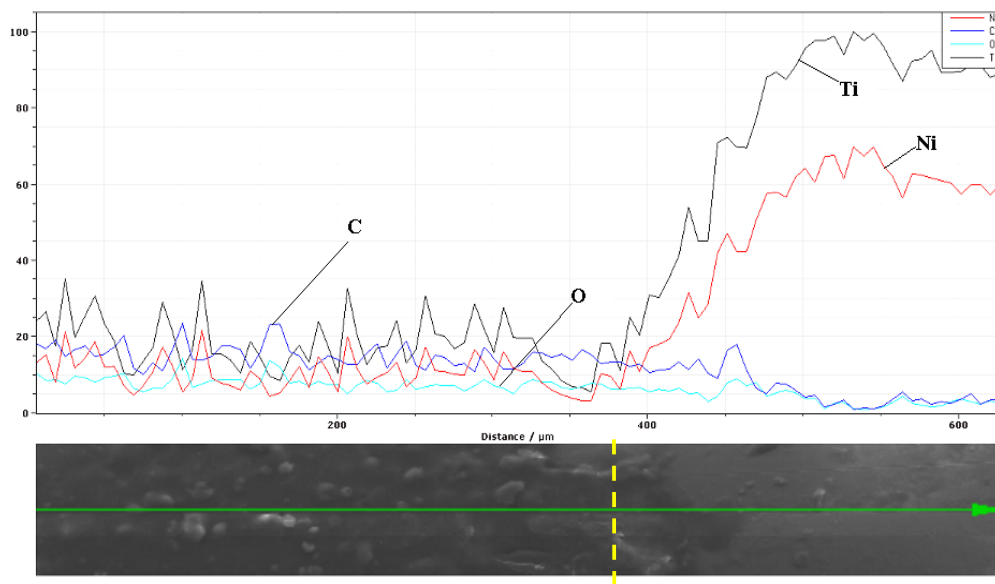


Fig. 5. Polymer layer and substrate chemical elements' distribution on a selected line.

In Fig. 6, the elemental mapping for a zone at the covered / uncovered border is presented. One can easily see the major presence of the C and O elements on the covered area, while the Ni and Ti signals dominate the

uncovered zone (the yellow color comes from addition of red and light green, i.e. simultaneous presence of Ni and Ti on the same analyzed spot).

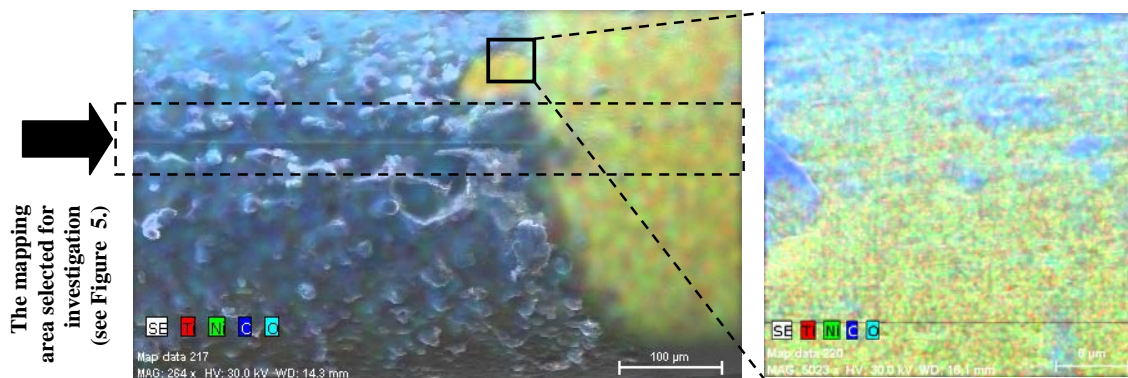


Fig. 6. Elemental (Ti, Ni, C and O) mapping of a covered / uncovered border zone.

4. Conclusions

Preliminary studies on the physico-chemical properties of PLLA thin films deposited by PLD on NiTi SMA substrates have been performed using Scanning Electron Microscopy. The PLD polymer thin films are “quasi-uniform” having nanoscale morphology with some micrometric inserted droplets. In order to associate the shape and dimensions of the included droplets with different experimental parameters, further fundamental research has to be considered. For instance, both space- and time-resolved optical and electrical methods can be applied to characterize the transitory plasma plume dynamics between target and substrate [13, 14].

Comparative chemical EDX analysis and elemental mapping of the PLD deposited films versus bulk polymer have been done. To preserve the bulk material properties, the stoichiometry is an important parameter to be taken into account. Our polymer thin films keep the 1:3 ratio of carbon : oxygen similar to the chemical composition of the polymer bulk.

References

- [1] S. F. Yang, K. F. Leong, Z. H. Du, C. K. Chua, *Tissue Engineering* **7**, 679 (2001).
- [2] A. Södergård, M. Stolt, *Prog. Polym. Sci.* **27**, 1123 (2002).

- [3] V. P. Paun, N. Cimpoesu, R. Hanu Cimpoesu, G. V. Muncelleanu, N. Fornu, M. Agop, *Materiale Plastice*, **47**(2), 158 (2010).
- [4] M. A. Paun, R. Cimpoesu Hanu, N. Cimpoesu, M. Agop, C. Baci, S. Stratulat, C. Nejnaru, *Materiale Plastice*, **47**(2), 209 (2010).
- [5] N. Cimpoesu, S. Stanciu, M. Meyer, I. Ionița, R. Cimpoesu Hanu, *J. Optoelectron. Adv. Mater.*, **12**(2), 386 (2010).
- [6] R. Cimpoesu Hanu, C. Baci, S. Stanciu, D. M. Aelenei, N. Cimpoesu, P. Paraschiv, in *B.P.I of Iași, LXVI (LX)*, 1 (2010).
- [7] T. H. Nam, T. Saburi, Y. Kawamura, K. Shimizu, *Mater. Trans. JIM* **31**, 262 (1990).
- [8] I. N. Mihailescu, P. Torricelli, A. Bigi, I. Mayer, M. Ilescu, J. Werckmann, G. Socol, F. Miroiu, F. Cuisinier, R. Elkaim, G. Hildebrand, *Appl. Surf. Sci.*, **248**, 344 (2005).
- [9] E. Gyorgy, P. Toricelli, G. Socol, M. Ilescu, I. Mayer, I. N. Mihailescu, A. Bigi, J. Werckmann, *J. Biomed. Mater. Res. A*, **71A**, 353 (2004).
- [10] S. Gurlui, M. Agop, P. Nica, M. Ziskind, C. Focsa, *Phys. Rev. E*, **78**, 026405 (2008).
- [11] C. Focsa, C. Mihasan, M. Ziskind, B. Chazallon, E. Therssen, P. Desgroux, J. L. Destombes, *J. Phys.: Condens. Matter* **18**, S1357 (2006).
- [12] C. Mihasan, M. Ziskind, E. Therssen, P. Desgroux, C. Focsa, *Chem. Phys. Lett.* **407**, 423 (2006).
- [13] S. Gurlui, M. Sanduloviciu, M. Strat, G. Strat, C. Mihasan, M. Ziskind, C. Focsa, *J. Optoelectron. Adv. Mater.*, **8**(1), 148 (2006).
- [14] C. Ursu, O. G. Pompilian, S. Gurlui, P. Nica, M. Agop, M. Dudeck, C. Focsa, *Appl. Phys. A*, **101**, 153 (2010).

*Corresponding author: nicanornick@yahoo.com